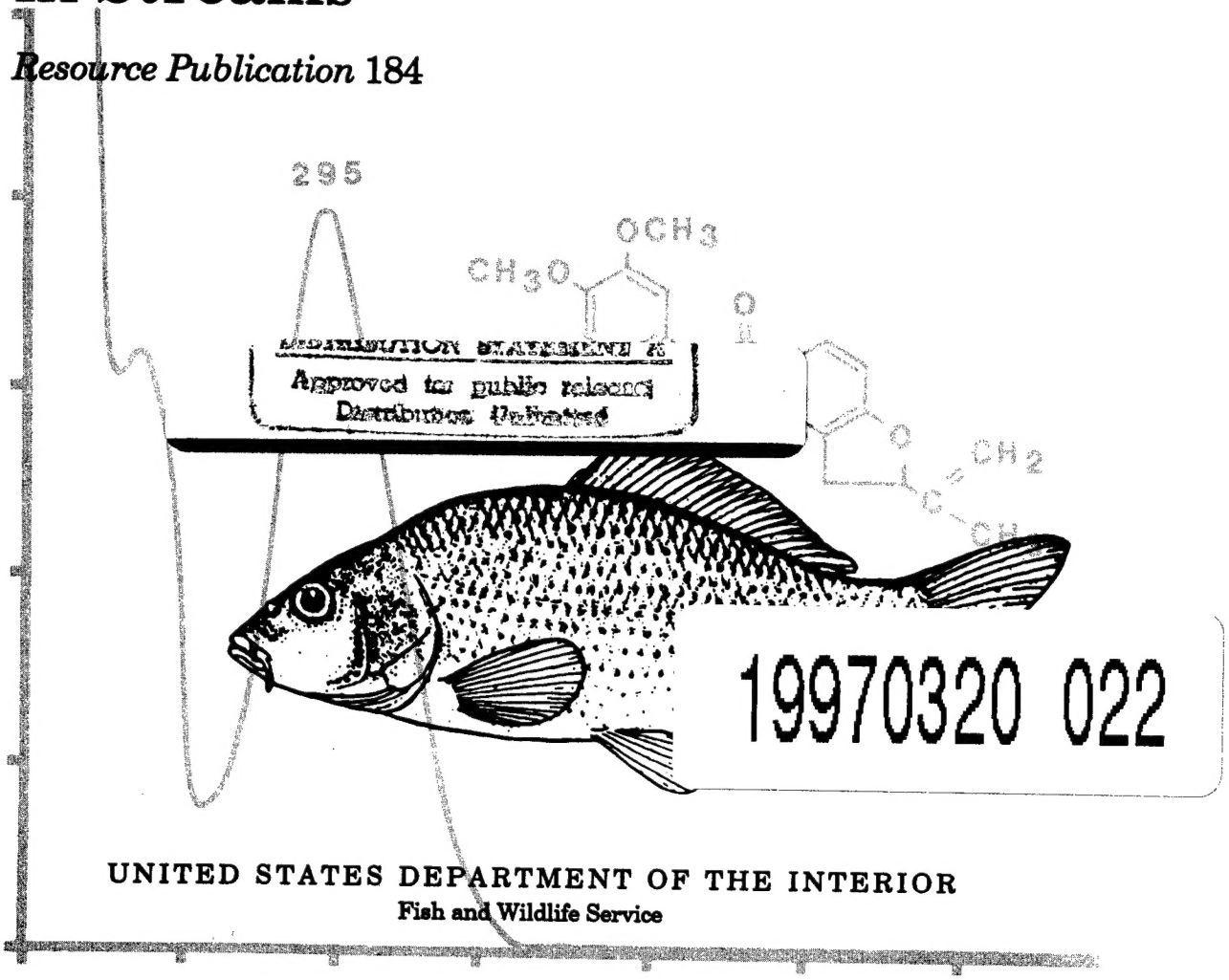
Effects of the Lampricide 3-Trifluoromethyl-4-Nitrophenol on the Pink Heelsplitter

Resource Publication 183

Methods for Detoxifying the Lampricide 3-Trifluoromethyl-4-Nitrophenol in Streams

Resource Publication 184



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Contents

Effects of the Lampricide 3-Trifluoromethyl-4-Nitrophenol on the Pink Heelsplitter

by

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Abstract. The lampricide 3-trifluoromethyl-4-nitrophenol (TFM) is used to selectively kill sea lampreys (*Petromyzon marinus*) in the tributaries of the Great Lakes. Over the years, TFM was tested most often on nontarget fishes and only occasionally on invertebrates, including freshwater mussels. We exposed pink heelsplitters (*Potamilus alatus*) to TFM concentrations and exposure times similar to those in lampricide treatments. Tests were conducted in water similar in quality to the Poultney River, New York, a stream that contains pink heelsplitters and is scheduled for lampricide treatment in 1991. Mussels were exposed to TFM for either 12 or 24 h and observed daily in well water for 14 days. Ninety percent of the mussels exposed to 3.5 mg/L of TFM for 12 h survived, however, only 50% of the mussels exposed to that concentration for 24 h survived. TFM seems to narcotize or anesthetize mussels. Mortality of mussels exposed to 3.5 mg/L TFM for 12 h seemed to be 60% immediately after treatment, but the actual mortality was only 10% after a 14-day recovery period. Our data suggest that several days of postexposure observation are required to correctly assess the effects of TFM on mussels.

Key words. TFM, toxicity, freshwater mussels, clams, nontarget organisms, sea lamprey.

The lampricide 3-trifluoromethyl-4-nitrophenol (TFM) is used extensively in tributaries of the Great Lakes to selectively kill larval sea lampreys (*Petromyzon marinus*) in the presence of other fishes (Applegate et al. 1958). The toxicity of TFM to nontarget fishes has been studied extensively, and the lampricide is generally considered nontoxic at concentrations that kill larval lampreys (Applegate et al. 1958, 1961; Applegate and King 1962).

Information on the toxicity of TFM to aquatic invertebrates is not nearly as abundant. Smith (1967) determined the toxicity of TFM to aquatic invertebrates in 15 orders. He found that *Hydra*, turbellarians, burrowing mayflies, and blackflies were sensitive, and snipe flies and dragonflies were the most resistant. Torblaa (1968) studied the invertebrate fauna in nine streams before and after a lampricide treatment and concluded that invertebrate numbers were reduced 1 week after treatment but returned to pretreatment levels of both abundance and species diversity within a year.

The effects of lampricide treatments on mollusks have not been fully determined because too few species were tested in previous studies to define trends. Gilderhus and Johnson (1980) noted that field crews reported dead snails and clams after about 21% of the stream treatments. They

also reported that Canadian personnel observed distressed clams with gaping valves during treatments, most of which recovered after the chemical bolt passed. The only published laboratory studies (Smith 1967; Maki et al. 1975) reported LC50 values of 10 to 17.5 mg/L TFM for unionid clams. The only other available reference about effects of the lampricide on mollusks is a study by Rye and King (1976) on a combination of 98% TFM and 2% Bayer 73. They determined that the 24-h LC50 for the mixture against spike (*Elliptio dilatata*, the lady-finger mussel of authors), was 4.7 mg/L. However, because Bayer 73 (Bayluscide) is a molluskicide, the toxicity from the combination should be greater than the toxicity from TFM alone.

Although public awareness and concern over the fate of freshwater mussels is increasing, information about the toxicity of TFM to mussels is limited. Our objective was to determine the mortality of a mussel species exposed to TFM at concentrations and exposure times of a proposed lampricide treatment in the Poultney River, New York. We chose the pink heelsplitter (*Potamilus alatus*) because the species is endemic at the proposed treatment site.

Materials and Methods

Static test procedures in this study followed those by the Committee on Methods for Toxicity Tests with Aquatic Organisms (1975) and ASTM Committee E-35 on Pesticides (1980). Mussels were exposed to a range of TFM concentrations in stainless steel tanks that contained 75 L of oxygen-saturated test water and 10 cm of substrate. In 24-h exposures, tanks were aerated to maintain dissolved oxygen levels above 60%. Substrate was collected from a dredge-material site on the upper Mississippi River (River Mile 688.7). The sediment was analyzed for particle size according to the method of Black (1965).

Reconstituted test water was prepared according to standardized procedures to produce water similar in quality to that of the Poultney River, New York (pH 7.9 ± 0.2, temperature 17 ± 1° C, alkalinity 105 ± 5 mg/L as $CaCO_3$; total hardness 105 ± 5 mg/L as $CaCO_3$, following standards by the Committee on Methods for Toxicity Tests with Aquatic Organisms 1975. The solutions were adjusted to the desired pH before the test and readjusted with chemical buffers every 6 h, if necessary, to maintain the intended pH level. Temperatures for the tests were regulated by immersing the test tanks in constant-temperature water baths. Water chemistry, dissolved oxygen (DO), temperature, and pH were monitored at 0, 6, 12, and 24 h.

Pink heelsplitters were collected by scuba divers from the upper Mississippi River (River Mile 709.8) at a depth of about 2 m and water temperature of 6° C. Mussels were held in flowing well water with substrate at the National Fisheries Research Center, La Crosse, Wis., for 1 week before treatment to ascertain mortality from handling. Specimens were fed daily during acclimation and after exposure by adding 250 mL of water with a bloom of green algae (*Selenastrum capricornutum*). A sample of 20 mussels, weighed and measured according to the method of Ball (1922), averaged 155.8 g in weight, 109.7 mm in length, and 90.2 mm in height. Mussels were acclimated to the test water for 24 h prior to exposure.

Twenty animals (10 in each of two tanks) were exposed to each concentration of TFM for either 12 or 24 h. After exposure, the mussels were transferred to flowing well water and monitored for recovery or delayed mortality. Observations on survival were recorded after 12 h of exposure and daily thereafter for 14 days.

Concentrations of TFM were selected from a regression chart of TFM toxicity provided by staff at the Marquette (Michigan) Biological Station. The chart predicted minimum lethal concentration (MLC) of TFM killing 100% of sea lamprey ammocoetes within 9 h at various water alkalinities, as well as maximum allowable concentration (MAC) at which no more than 25% of the nontarget fishes are affected within 24 h (Kanayama 1963; Seelye et al 1988). Field-grade TFM (41% active ingredient, Batch 1, CN-NR CO2290601) produced in 1989 by the Hoechst Chemical Company, Frankfurt, Germany, was tested at concentrations of 0 mg/L (control), MLC × 0.5 = 1.75 mg/L, MLC × 1.0 = 3.5 mg/L, MLC × 1.5 = 5.25 mg/L, and MAC = 7.4 mg/L. Stock solutions were prepared by diluting weighed amounts of TFM with deionized water; aliquots of these stocks were pipetted into the test vessels to produce the desired concentrations.

TFM concentrations were measured by a modified high-performance liquid chromatography method of Dawson (1982) at 0, 12, and 24 h after the initial exposure. Samples were filtered with 0.45 µm Acrodiscs to remove particulate matter and then analyzed with a Waters Associates, Inc., Model 712 WISP Auto Sampler, two Model 510 pumps, Model 680 gradient controller, Model 484 spectrophotometer, and a Model 745 data module. Operating conditions were as follows: stationary phase—30 cm × 3.9 mm WatersµBondapak C_{18} column; mobile phase—65% methanol, 35% 0.01-M acetate buffer; flow rate—2.0 mL/min; chart speed—2.0 cm/min; wavelength—220 nm; and attenuation—0.10 absorption units. Peak area was measured with a Model 754 Data Module that was calibrated with an external standard. Sample concentrations were quantified against a linear three-point calibration curve. Retention time of TFM was 3.75 min.

Results

Chemical and Physical Exposure Characteristics

Chemical characteristics of the test water were maintained within the ranges for water of the Poultney River, New York (Table 1). Dissolved oxygen levels decreased about 2.5 mg/L during the 12-h exposure, however, DO concentrations remained greater than 60% of saturation throughout the duration of the exposure. This decrease in DO was accompanied by a reduction in pH of about 0.2 units, probably from respiratory CO_2 produced by the test animals. Water temperatures remained constant at 17° C throughout the tests. Total alkalinity and total hardness were between 100 and 117 mg/L (as $CaCO_3$).

TFM concentrations in the test tanks (Table 2) were within 97% of the calculated value at time 0 (immediately after the solutions were mixed). Concentrations had decreased by 16% after 12 h, probably from adsorption of TFM onto the substrate (Dawson et al. 1986). Little additional TFM was lost from the test solutions between 12 and 24 h (which indicated that most adsorption probably occurred early in the exposures).

Particle size characterization of the sediment indicated that the substrate was 99% sand and 1% silt and clay (Table 3). Sediments that are predominately sand, such as from the upper Mississippi River site, are considered uncontaminated and do not alter the toxicity of the lampricide (Marking et al. 1981).

Biological Response

The mussels showed varying degrees of stress that were directly associated with increased concentrations of TFM. During the acclimation period,

Table 1. *Mean (± SD) test-water characteristics[a] during laboratory exposure of pink heelsplitters to TFM for 12 or 24 h.*

Observation time (h)	Dissolved oxygen (mg/L)	pH	Concentration (mg/L as $CaCO_3$) Hardness	Alkalinity
12-h exposure				
0	9.15 (±0.20)	8.03 (± 0.16)	107 (± 0.8)	100 (± 1.3)
6	7.39 (±0.30)	7.81 (± 0.11)	112 (± 2.1)	101 (± 2.4)
12	6.61 (±0.64)	7.84 (± 0.09)	114 (± 2.4)	102 (± 1.8)
24-h exposure				
24	8.45[b] (±0.26)	7.94 (± 0.01)	111 (± 2.1)	101 (± 1.4)

[a] Water temperature was 17° C in all tanks.

[b] Experimental tanks for 24-h exposures were aerated.

Table 2. *Concentration of TFM in test water with time following laboratory treatment, as determined by high-performance liquid chromatography.*

Calculated concentration at application (mg/L)	Measured concentration of TFM (mg/L) in pairs of tanks (A and B) at time after treatment					
	0 h		12 h		24 h	
	A	B	A	B	A	B
12-h exposure						
1.75	1.74	1.85	1.75	1.79	—	—
3.50	3.75	3.53	3.38	3.35	—	—
5.25	5.14	5.15	4.90	4.92	—	—
7.4	7.08	7.22	6.90	6.95	—	—
24-h exposure						
3.50	3.47	3.53	3.22	3.21	3.21	3.41
5.25	5.16	5.01	4.73	4.72	4.70	4.71

Table 3. *Particle size characterization of sediment (dredged from Mississippi River Mile 688.7)[a] serving as burrowing substrate for sea lamprey ammocoetes in laboratory experiments.*

Soil type	Particle size (mm)	Sample I Total weight (g)	Sample I Total weight (%)	Sample II Total weight (g)	Sample II Total weight (%)	Mean (%)
Very coarse sand	1–2	2.0	4.0	2.4	4.8	4.4
Coarse sand	0.5–1	9.4	18.8	9.7	19.4	19.1
Medium sand	0.25–0.5	30.4	60.8	30.4	60.8	60.8
Fine sand	0.125–0.25	7.4	14.8	6.9	13.8	14.3
Very fine sand	0.0625–0.125	0.2	0.4	0.2	0.4	0.4
Coarse silt	0.005–0.0625	0.5	1.0	0.3	0.6	0.8
Fine silt and clay	0.002–0.005	0.1	0.2	0.1	0.2	0.2

[a] Based on two 50-g samples.

all the mussels burrowed into the sediment and established themselves in a normal upright position; control organisms remained burrowed throughout the test and recovery periods. Most animals that were exposed to TFM emerged from the sediment and displayed the foot, possibly because of irritation from the chemical (Fig. 1). After 12 h of exposure to TFM, 20% of the mussels exposed to 1.75 mg/L, 60% of those exposed to 3.5 mg/L, and 100% of those exposed to 5.25 or 7.4 mg/L exhibited an extended foot and gaped valves and did not respond to external stimuli (Fig. 2).

After 12 h in fresh, aerated well water, 70% of the mussels exposed to 1.75 mg/L TFM for 12 h had burrowed into the sediment and an additional 25% had not burrowed but responded to external stimuli. Of those exposed to 3.5 mg/L TFM, 50% responded to external stimuli; the valves of the remaining mussels were either tightly closed or gaped. Only one of the mussels exposed to 5.25 or 7.4 mg/L TFM responded to external stimuli.

After 12 h in fresh water, mussels exposed for 24 h to 3.5 and 5.25 mg/L of TFM showed responses similar to those of mussels exposed to the higher concentrations for 12 h. In the 3.5 mg/L group, 10% of the mussels had burrowed into the sediment and 20% had not burrowed but responded to external stimuli; the valves of the remaining 70% were gaped. None of the organisms exposed for 24 h to 5.25 mg/L of TFM was responsive.

Seven days after removal to fresh water, 95% of the mussels exposed to 1.75 mg/L TFM for 12 h were responsive and reacted similarly to the control organisms. Of those exposed to 3.5 mg/L, 55% had burrowed into the sediment and an additional 35% responded to external stimuli. No response was observed in 75% of the mussels exposed to 5.25 mg/L of TFM and 80% of those exposed to 7.4 mg/L of TFM. Mussels exposed to TFM for 24 h

Fig. 1. Pink heelsplitters in the primary stage of TFM intoxication; they have abandoned the normal buried position and lie on the substrate with foot extended.

were more severely affected; 50% of those exposed to 3.5 mg/L responded normally after 7 days, but only 5% of those exposed to 5.25 mg/L responded to external stimuli.

Fourteen days after exposure, 90% of the mussels exposed to 3.5 mg/L of TFM for 12 h survived, but less than 30% of those exposed to 5.25 mg/L for 12 h or 7.4 mg/L survived (Table 4). As expected,

Fig. 2. Pink heelsplitters in the secondary stage of TFM intoxication; they gape their valves and no longer respond to external stimuli.

Table 4. *Survival of pink heelsplitters 14 days after exposure to selected concentrations of TFM for 12 or 24 h in reconstituted water at 17° C.*

Exposure time and concentration (mg/L)	Survival (%) Group I[a]	Group II	Mean
12-h exposure			
0 (control)	100	100	100
1.75	100	90	95
3.50	90	90	90
5.25	40	20	30
7.40	10	10	10
24-h exposure			
3.50	60	40	50
5.25	10	0	5

[a]Two groups of 10 each mussels were exposed at each concentration.

24-h exposures to TFM were more toxic to mussels than 12-h exposures; a concentration of 3.5 mg/L killed 50% of the mussels exposed for 24 h compared to only 10% of the mussels exposed to 3.5 mg/L for 12 h.

Discussion

The Poultney River was scheduled to be treated with TFM in the fall of 1991 to control sea lamprey larvae. The selected MLC (3.5 mg/L) in waters with chemical characteristics similar to the Poultney River is based on the concentration of TFM that should kill sea lamprey ammocoetes but only minimally affects nontarget organisms (Kanayama 1963). Common maximum treatment concentrations are 1.5 × MLC to counteract dilution and attenuation of the TFM bolt to less than the MLC as the bolt passes between application sites. However, planned treatment concentrations in the Poultney River ranged only from 0.8 × MLC (2.8 mg/L) to no greater than MLC to protect all sensitive nontarget organisms and satisfy special conditions of the environmental impact statement.

Comparison of the results from our study with existing data revealed that the pink heelsplitter is sensitive to TFM. Concentrations of TFM at or above 5.25 mg/L produced significant mortalities. Although treatment of the river at 3.5 mg/L may cause some mortality, TFM should not permanently affect the mussel population; 90% of the mussels survived exposure to this level of TFM in our laboratory study. In general, laboratory studies demonstrate worst-case conditions. In the field, the toxicity of chemicals to endemic organisms is usually less.

Our observations reflect the opinions of Gilderhus and Johnson (1980) and of Canadian sea lamprey control personnel that TFM treatments probably cause some mortality among sensitive mussel species. Some mussels were reported dead in 21% of the recorded posttreatment surveys, however, the surveys were conducted shortly after the stream treatments, and many nonresponsive mussels that were considered dead might have recovered and significantly lowered reported mortality. Without the 14-day recovery period in fresh water, we might have concluded that 60% of the mussels were killed by exposure to 3.5 mg/L of TFM rather than the 10% that were actually killed. Our data suggest that correct assessment of the effects of TFM on mussels requires postexposure observation of several days.

Other invertebrates are also narcotized or anesthetized by TFM. Kawatski et al. (1975) noted that some invertebrates exposed to TFM were immobilized and appeared dead, but most recovered when placed in fresh water. Gilderhus and Johnson (1980) reported that mussels with valves gaped during lampricide treatments recovered after the bolt of chemical passed. Although TFM treatments seem to immediately stress mussels in the stream, the effect on the mussel population is probably much less than initially expected. Field studies reported by Gilderhus and Johnson (1980) indicate that populations of invertebrates in treated streams quickly recover from the effects of TFM. Many animals that appear dead in the posttreatment population subsequently recover.

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Methods for Detoxifying the Lampricide 3-Trifluoromethyl-4-Nitrophenol in a Stream

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Abstract. Two methods to detoxify the lampricide 3-trifluoromethyl-4-nitrophenol (TFM) were tested in the laboratory. Application of 30 to 50 mg/L of activated carbon, applied as an aqueous slurry, removed enough TFM from the water to detoxify most sea lamprey control treatments. Because the toxicity of TFM decreases as the pH of water increases, we also tested the application of sodium hydroxide (NaOH) to raise the pH of the water. Raising the pH by 1.5 units partly detoxified concentrations of TFM applied in lamprey control. A small tributary of the Sturgeon River, Delta County, Michigan, was treated with 6.5 mg/L TFM. Caustic soda to raise the pH of the stream was applied a short distance downstream. All caged rainbow trout (*Oncorhynchus mykiss*) died in the reach with TFM but none died downstream of the raised pH. Raising the pH of the stream detoxified TFM enough to reverse an ongoing major kill of nontarget fishes.

Key words. Toxicity, detoxification, lampricide, activated carbon, sodium hydroxide, pH, sea lamprey.

The lampricide 3-trifluoromethyl-4-nitrophenol (TFM) is routinely applied to tributaries of the Great Lakes to selectively kill larval sea lampreys (*Petromyzon marinus*) in the presence of other fishes. The concentration that is toxic to larval sea lampreys, but safe for other fishes, is determined by on-site toxicity tests or derived from known water chemistry–toxicity correlations for TFM. Occasionally, the treatments kill substantial numbers of nontarget fishes. At present, no method exists to detoxify TFM in the stream. Fish kills cause environmental harm and negative public reaction that adversely affect the control of lampreys.

To address this problem, we tested two potential methods of detoxification in the laboratory and one in the field. The first method, application of a slurry of activated carbon, was chosen because activated

carbon is known to remove many organic chemicals from water (Davies et al. 1973; Dawson et al. 1976). The second, raising the pH of the water with sodium hydroxide (NaOH), was based on previous studies showing that TFM is less toxic in waters with higher pH (Marking and Olson 1975; Bills et al. 1988). The latter method was tested in a small stream in the Upper Peninsula of Michigan to assess the feasibility of its application in the field.

Methods

Activated Carbon

Two grades of powdered activated carbon (WPH and WPL), recommended for their adsorptive efficiency, were obtained from the Calgon Carbon Corp., Pittsburgh, Pa., and evaluated for their efficiency in adsorbing TFM. Selected amounts of carbon were added to water solutions containing 10 mg/L of TFM. After 15 min, samples were collected, filtered, and analyzed for concentrations of TFM. The most efficient of these carbons, WPH, was tested further. Twenty to 50 mg/L of WPH-grade carbon were added to 1-L solutions of water containing 10 mg/L of TFM and stirred every 10 min. Samples were taken after 15, 30, and 60 min, filtered, and analyzed for TFM with spectrophotometry.

The amount of carbon that detoxified various concentrations of TFM was determined in 12-h toxicity tests with fathead minnows (*Pimephales promelas*). Test vessels were glass jars with 15 L of soft reconstituted water (total hardness 40–48 mg/L; total alkalinity 30–35 mg/L) at 12° C. Each test was started by first adding TFM and then carbon volumetrically as a water slurry; after 15 min, fishes that had been acclimated for 24 h to the test water and temperature were added. Fish mortality was compared in tests with and without carbon.

Alteration of pH

Laboratory Tests

The fish species and conditions for tests with various pH were the same as for tests with activated carbon, except that soft and hard water were used (total hardness, 160–180 mg/L; total alkalinity, 110–120 mg/L) and the fishes were acclimated for 24 h in the jars before TFM was added. The pH was then raised 1.0 or 1.5 units by adding NaOH. The 12-h mortality from these tests and from a series of tests without raised pH were compared.

Field Tests

We tested raising the pH of the water to detoxify TFM in a small tributary of the Sturgeon River in Delta County, Michigan. During the treatment, the stream had a discharge of 0.06 m^3/s (2.2 cfs), total hardness of 94 mg/L, total alkalinity of 78 mg/L, temperature of 16–19° C, and pH of 7.2–7.4.

We treated the stream at a TFM concentration of 6.5 mg/L, a level that is toxic to nontarget fish species. Field-grade TFM (36% active ingredient) was metered into the stream with a peristaltic pump for 6 h. About 0.4 km downstream from the TFM application, NaOH was applied to raise the pH of the stream. The NaOH (commercial grade, 50% caustic soda solution) was diluted 10:1 with stream water in a plastic tank and metered into the stream with a peristaltic pump. The pH was raised about 1.8 units (Table 1).

Rainbow trout (*Oncorhynchus mykiss*) of 9.1 cm mean length and larval sea lampreys of 10.3-cm mean length were caged separately in the stream. Ten each were caged upstream from the TFM application as controls, 30 each were caged between the TFM and NaOH applications, and 30 each were caged downstream from the NaOH application. Trout numbered 10 per cage and lampreys 10 or 20 per cage. Each cage with lampreys contained a pan with sand for burrowing.

Results and Discussion

Activated Carbon

Laboratory tests showed that WPH-grade activated carbon efficiently removed TFM from water. The amount of removed TFM was a function of time and the concentration of carbon (Table 2). Results from the laboratory tests with fathead minnows were consistent with data from the chemical analysis. Twenty to 50 mg/L of carbon detoxified TFM

Table 1. *Concentration of TFM in stream water and pH of the stream before (upstream) and after (downstream) addition of sodium hydroxide to detoxify TFM in a tributary to the Sturgeon River, Delta County, Michigan.*

Upstream				Downstream		
	TFM	pH			TFM	
Time	concentration (mg/L)	Above NaOH application	Below NaOH application	Time	concentration (mg/L)	pH
1030	0.0	7.2	9.3	1200	0.0	7.6
1100	7.0	7.4	9.1	1300	0.0	7.9
1130	6.5	7.4	9.1	1400	3.6	8.1
1200	6.1	7.4	9.2	1500	4.8	8.1
1230	6.7	7.3	9.2	1600	4.8	8.1
1300	6.4	7.2	9.1	1700	5.0	8.1
1330	6.5	7.4	9.1	1800	5.1	8.1
1400	6.2	7.4	9.1	1900	5.2	8.1
1430	6.3	7.4	9.1	2000	2.7	8.1
1500	6.4	7.3	9.1	2100	0.6	7.8
1530	6.6	7.3	9.1	2200	0.0	7.8
1600	6.7	7.4	9.1	2300	0.0	7.7

concentrations as high as 8 mg/L, a level normally toxic to nontarget fishes in streams with similar water characteristics (Table 3). Carbon reduced the concentration of TFM to a nontoxic level, but did not remove it completely.

Increased pH

Laboratory Tests

Raising the pH of the water was highly effective for detoxifying TFM. An increase of 1.0 to 1.5 pH units detoxified TFM at concentrations that exceed most of those used in stream treatments (Table 4). Although an increase of 1 pH unit renders most treatment levels of TFM nontoxic, raising the pH by 1.5 units is advisable to offset the dispersion, dilution, and metabolic processes in the stream. These processes tend to return the pH to the ambient level at which TFM is toxic to fishes.

In soft water, the amount and cost of detoxification are about three times greater for carbon than for NaOH (Table 5). In hard water, the amount and cost of detoxification are similar, but the application of NaOH is much easier. NaOH can be applied in the same formulation (50% solution) that is

Table 2. *Adsorbtion of TFM from 10-mg/L solutions by activated carbon (analyzed by spectrophotometry).*

Activated carbon concentration (mg/L)	Amount of TFM adsorbed (mg/L) with time of exposure		
	15 min	30 min	60 min
20	2.3	—	—
30	3.1	3.5	4.1
40	3.5	4.2	5.0
50	4.4	4.4	5.8

Table 3. *Concentrations of TFM detoxified by activated carbon in 12-h laboratory tests with fathead minnows* (Pimephales promelas) *in soft water at 12°* C.

Activated carbon (mg/L)	Nonlethal TFM concentration with activated carbon[a] (mg/L)
20	5
30	5
40	7
50	8

[a] Lethal concentration of TFM without activated carbon was 4 mg/L.

Table 4. *Toxicity of TFM with pH increase in soft and hard water at 12° C in 12-h laboratory tests with fathead minnows* (Pimephales promelas).

Initial pH	Lethal TFM concentration at initial pH (mg/L)	pH after adjustment	Non-lethal TFM concentration after adjustment (mg/L)
Soft water			
7.6	3	8.6	5
7.6	5	9.1	10
Hard water			
8.1	9	9.1	10[a]
8.1	10	9.6	28[a]

[a] Highest concentration tested.

Table 5. *Approximate quantity of activated carbon or sodium hydroxide (NaOH) and cost per hour to detoxify TFM within a stream flow of 1 m^3/s.*

Water hardness and units	Activated carbon	NaOH[b]
Soft water[a]		
Rate	30 mg/L	—
Amount	108 kg	34 kg[c]
Cost in 1990	$233	$84
Hard water		
Rate	50 mg/L	—
Amount	180 kg	122 kg[c]
Cost in 1990	$388	$307

[a] Total hardness 40–48 mg/L (vs. 160–180 mg/L in hard water).
[b] Amount of 50% solution required to raise the pH 1.5 units.
[c] 1 kg = 0.65 L of 50% solution.

purchased, whereas carbon requires producing a slurry because it is flocculent, and may drift easily in a slight breeze. Because it is less costly and simpler than adding carbon, we chose to test the adjustment of pH in the field.

Field Tests

All caged trout and larval lampreys between the TFM and NaOH application points died in less than 1 h, but none died in the 3.2-km detoxified reach of the stream (Table 6). The mortality of larval sea lampreys, which are sensitive to much lower concentrations of TFM, was 10% at the upper end of the detoxified reach and 100% near the mouth, 3.2 km downstream. A 40% increase in volume of flow between the application point and the mouth decreased the TFM concentration from 6.5 to 4.4 mg/L and the pH by 1.0 unit. The data suggest that the mortality of larval sea lampreys increased at the mouth because the pH returned to a level where TFM is toxic to them even at the lower concentration.

Table 6. *Mortality of caged larval sea lampreys* (Petromyzon marinus) *and rainbow trout* (Oncorhynchus mykiss) *in a stream treated with the lampricide TFM and then with sodium hydroxide to raise pH in a tributary to the Sturgeon River, Delta County, Michigan.*

Cage placement	Mortality (%) Larval sea lampreys	Mortality (%) Rainbow trout
Upstream (controls)	0	0
Between TFM and NaOH application point	100	100
0.8 km below NaOH application point	10	0
3.2 km downstream	100	0

The application of NaOH is simple in a small stream but may be more difficult in large streams. Detoxifying a stream with an alkalinity of 80 mg/L, as in the trial stream, requires 50 L/h of 50% NaOH per m^3/s of flow. Thus, 400 L of NaOH are needed to detoxify an 8-h bolt of TFM at a flow of 1 m^3/s.

Our trial in the field demonstrated that counteracting the toxicity of TFM by raising the pH of the stream is feasible. However, the method becomes logistically more difficult as the alkalinity, hardness, and volume of the stream increase. Whether the method is practical and applicable must be answered by personnel in sea lamprey control who carry out the field applications. In any case, raising stream pH may detoxify TFM enough to reverse or diminish the severity of a major fish kill in progress.

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A list of current *Resource Publications* follows.

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